Electronic spectroscopy of *s-trans* 1,3-butadiene by electron impact*

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The electron impact excitation of 1,3-butadiene has been studied experimentally at impact energies of 20, 35, and 55 eV and scattering angles from 10° to 85°. The energy and angular dependences of the cross section ratios are used to identify the nature of the excited states. Two transitions with maxima at 3.22 and 4.91 eV are identified as singlet→triplet transitions. Comparison with theoretical calculations indicates that these are due to the 1^3B_u and 1^3A_g states, respectively. Their significance for the photochemistry of this molecule is discussed. The optically allowed $\tilde{X}\ ^1A_g \rightarrow 1^1B_u(N \rightarrow V_1)$ transition is observed with a maximum at 5.92 eV. An additional transition appears between 6.9 and 7.8 eV with vibrational features at 7.09, 7.28, and 7.46 eV. The optical absorption in this region was originally attributed to a $^1A_1$ state of the *s-cis* molecule and subsequently to a Rydberg state or to a ^1A_g state of the *s-trans* molecule. On the basis of intensity arguments and the angular dependence of the cross section ratios, we suggest that it may instead be due to the $\tilde{X}\ ^1A_g \rightarrow 2^1B_u$ transition of the *s-trans* molecule. Rydberg transitions are observed at 8.00 and 8.18 eV. Two broad transitions are also seen beyond the first ionization potential with maxima at 9.50 and 11.00 eV. The results of this study are in good agreement with recent *ab initio* configuration interaction (CI) calculations, and give support to the analysis of the valence excited states in terms of a "molecules-in-molecules" approach. This is consistent with recent interpretations of the resonance energy and reactivity of this molecule and differs from the older classic model of extensive delocalization in the π electron system.

1. INTRODUCTION

1,3-butadiene is an important prototype molecule because it is the simplest example of a case where resonance may take place between two conjugated double bonds. Its absorption spectrum has been used[1] as a model for the analysis of the spectra of open-chain conjugated dienes and conjugated polyenes and their derivatives, such as Vitamin A and the carotenoids. In this model, the π electrons occupy delocalized molecular orbitals which spread over the conjugated double bond frame of the molecule. The lowest singlet → singlet transition shifts to longer wavelengths as the number of conjugated double bonds increases, in analogy with the energy levels of a particle in a one-dimensional box. A contrasting view[2–5] considers the double bonds to be localized and only weakly interacting.

Although the optical absorption spectrum of butadiene was first reported[6] in 1934, there remain significant differences among interpretations of the spectrum. In addition, optically forbidden transitions in this molecule have been detected by the oxygen enhancement,[7] threshold electron impact excitation,[8] and ion impact excitation[9] techniques, which are in disagreement with one another. Finally, there are excited states of uncertain identity[10] which participate in the photochemistry of 1,3-butadiene.

Low energy electron impact spectroscopy at variable scattering angles has proved[11] to be a powerful tool for the detection and identification of optically forbidden electronic transitions in atoms and molecules. An experimental study of 1,3-butadiene using this technique was undertaken to investigate such optically forbidden transitions in this molecule in order to shed light on the several matters mentioned above. The excitation spectrum was studied at impact energies of 20, 35, and 55 eV and scattering angles from 10° to 85°. Energy-loss features as high as 12 eV above the ground state were investigated.

In what follows, we summarize previous theoretical and experimental studies of the electronic spectrum of 1,3-butadiene, give a description of the experimental methods used in this study, present the results and discussion, analyze their meaning for the photochemistry of this molecule, and give final conclusions.

2. PREVIOUS STUDIES OF THE ELECTRONIC STATES OF 1,3-BUTADIENE

2.1. Theoretical Calculations

Mulliken[12] qualitatively analyzed the excited states of butadiene using the molecular orbital method. He considered only the π electrons and formed the MO's from single $2p$ atomic orbitals on each carbon atom. The four lowest energy transitions were designated as $N \rightarrow V_1$, V_2, V_3, V_4. In terms of the symmetry point group (C_{2h}) for *s-trans* butadiene (*trans* with respect to the single bond), the excited states would be ^1B_u, ^1A_g, ^1A_g, ^1B_u. It should be noticed that the middle two states

are symmetry-forbidden ($g \not\rightarrow g$) for excitation from the ground state, $\tilde{X}\,^1A_g$. If butadiene were *s-cis* (C_{2v}), however, transitions to these states would be optically allowed ($\tilde{X}\,^1A_1 \rightarrow {}^1A_1$).

One of the earliest (semi) *ab initio* calculations on the π-electron states of butadiene was by Parr and Mulliken.[13] The 26 inner electrons (the carbon 1*s*, CC σ bonding, and CH bonding electrons) were replaced by an effective potential and only the π electrons were studied explicitly. The molecular orbitals were taken as linear combinations of Slater type $2p\pi$ atomic orbitals. They then solved the Hartree–Fock equations for the ground state by the self-consistent field method, and assumed that the excited state orbitals are the same as those of the ground state. This calculation involved no explicit semiempirical adjustment of the necessary multicenter integrals, although approximations were made in their evaluation.

These *ab initio* calculations were only in qualitative agreement with experiments. In an attempt to improve this agreement and simultaneously simplify the calculation, Pariser and Parr[14] used a semiempirical approach within the framework of delocalized molecular orbital π-electron theory. Several additional calculations of this kind were made.[15–18] Improved agreement with the optically allowed $\tilde{X}\,^1A_g \rightarrow 1\,^1B_u$ ($N \rightarrow V_1$) transition energy over that of the Parr–Mulliken calculation resulted. However, the position of the low-lying triplet states varied significantly from calculation to calculation.

Recently, two high quality *ab initio* configuration interaction calculations[2,19] of the excited states of 1, 3-butadiene have been performed. Hosteny *et al.*,[2] using about 1800 space configurations, find that the two lowest ^1B_u states of the *s-trans* isomer are diffuse in nature, and interpret their results in terms of a molecules-in-molecules model.[3,4] Shih *et al.*[19] performed similar calculations on both the *s-trans* and *s-cis* molecules, and allowed for partial relaxation of the sigma core. They also obtain a diffuse character for the two lowest ^1B_u states and, in addition, for the first time in an *ab initio* calculation, place the vertical excitation energy of the $2\,^1A_g$ state above that of the $1\,^1B_u$ state. The results of these two calculations are given in Table I and discussed further in Sec. 4.

2.2. Optical Spectroscopy

The optical spectrum of butadiene has been reported by Scheibe and Grieneisen,[6] Price and Walsh,[20] and later authors.[21–23] Butadiene begins to absorb at or below 5.4 eV. Four broad strong bands appear between 5.7 and 6.3 eV with a maximum intensity[24] at 5.92 eV[22,23] and have a vibrational spacing of 1440 cm^{-1}. Mulliken[12] has assigned these features as arising from the $\tilde{X}\,^1A_g \rightarrow 1\,^1B_u(N \rightarrow V_1)$ transition.

A number of fairly sharp narrow features occur[6,20] at 6.25, 6.66, 6.81, 7.04, 7.06, 8.00, and 8.17 eV and are listed by Herzberg[25] as separate electronic transitions because of their irregular appearance. Two Rydberg series above 8 eV have been analyzed,[20] and both converge to the first ionization potential at 9.06 ev. This agrees well with the values of both Watanabe[26] and Al-Joboury and Turner,[27] who obtained ionization potentials of 9.07 and 9.08 eV, respectively. There is also a broad maximum[20] observed beyond the first ionization potential at 9.55 eV.

A series of diffuse bands, located between 7 and 7.7 eV, is about 20% as intense as those of the 5.92 eV state. Mulliken[1] assigned this band system as an $\tilde{X}\,^1A_1 \rightarrow {}^1A_1(N \rightarrow V_{2,3})$ transition of the *s-cis* conformer.

The low-lying triplet states of butadiene were investigated optically by Evans[7] using the high pressure oxygen perturbation technique. Two broad absorptions with maxima at 3.2 and ~3.9 eV were assigned to triplet states with apparent $0 \rightarrow 0$ transitions at 2.58 and 3.56 eV, respectively. However, Evans[28] has since pointed out that the second absorption band is in fact due to simultaneous transitions in butadiene ($\tilde{X}\,^1A_g \rightarrow 1\,^3B_u$) and oxygen ($X\,^3\Sigma_g^- \rightarrow a^1\Delta_g$).

Brongersma *et al.*[8] have performed trapped electron studies of 1, 3-butadiene. There is a broad feature from 2.5 to 4.5 eV with a maximum at 3.8 eV and a "very vague shoulder" at 3.3 eV. An additional very weak narrow feature is seen at 4.8 eV. Both features are tentatively identified as singlet → triplet transitions.

Wei[29] has studied the 90° electron scattering spectrum of butadiene at impact energies of 30 to 50 eV. The spectrum shows strong bands at 5.9 and 9.7 eV. No states were observable below 5 eV because of low energy resolution and the resulting large tail of the elastic peak.

2.3. Ion Impact Spectroscopy

Moore[9] has performed ion impact energy-loss spectroscopic studies of butadiene using both H^+ and He^+ at 3 keV impact energy. Up to a few keV impact energies, the duration of a collision is long enough to permit electron exchange between the ion and the target molecule. Thus, excitation of molecules to spin forbidden states is often observed. The appearance of a transition in the He^+ impact spectra and its absence in the H^+ impact spectra, where no exchange is possible, is sug-

TABLE I. Excited electronic states of *s-trans* 1, 3-butadiene.

State	Nature of state	Theory		Previous experimental results				Present experiments	
		Shih[a] *et al.*	Hosteny[b] *et al.*	Optical	Trapped[c] electron	90° Electron[d] impact	Ion[e] impact	Peak	Range of band
$1\,^3B_u$	Valence[a,b]	3.24	3.45	3.22[g] (2.58)[h]	3.3	•••	3.2	3.22 ± 0.04	2.5–4.5[l]
$1\,^3A_g$	Valence[a,b]	4.95	5.04	•••	3.8 4.8	•••	4.9	4.91 ± 0.03	4.0–5.5[l]
$1\,^3B_g$	Rydberg	6.17	•••	•••	•••	•••	•••	•••	•••
$1\,^1B_g$	Rydberg	6.24	•••	•••	•••	•••	•••	•••	•••
$1\,^3A_u$	Rydberg	6.48	•••	•••	•••	•••	•••	•••	•••
$1\,^1A_u$	Rydberg[a]	6.50	•••	6.66[f]	•••	•••	•••	•••	•••
$1\,^1B_u$	Diffuse[a,b]	6.60	7.05	5.92[i]	~6	5.9	6.1	5.92 ± 0.02	5.0–6.9
$2\,^1A_g$	Double[b] excitation valence	6.67	6.77	6.25[f]	•••	•••	•••	•••	•••
$2\,^3A_u$	Rydberg	6.67	•••	6.81[f]	•••	•••	•••	•••	•••
$2\,^1A_u$	Rydberg[a]	6.76	•••	•••	•••	•••	•••	•••	•••
$2\,^3B_g$	Rydberg	7.29	•••	•••	•••	•••	•••	•••	•••
$2\,^1B_g$	Rydberg	7.31	•••	•••	•••	•••	•••	•••	•••
$2\,^3B_u$	Diffuse[b]	7.55	7.14	•••	•••	•••	•••	•••	•••
$3\,^1A_g$	Diffuse[b]	7.79	7.82	•••	•••	•••	•••	•••	•••
$3\,^3B_u$	Double[b] excitation valence	7.92	8.08	•••	•••	•••	•••	•••	•••
$2\,^1B_u$	Diffuse[a,b]	7.98	8.06	7.27[j,k]	7.2[k]	•••	7.3[k]	7.09 ± 0.02 7.28 ± 0.02[k] 7.46 ± 0.02	6.9–7.8

$\tilde{G}$	Rydberg[f]	...	...	8.00[f]	...	...	...	8.00 ± 0.02	...	
$\bar{H}$	Rydberg[f]	...	...	8.17[f]	...	...	...	8.18 ± 0.02	...	
$n\,^1B_u$	Rydberg	9.16	...	...	...	...	...	...	...	
$\bar{I}$	Superexcited	...	...	9.55[f]	...	9.6	...	9.50 ± 0.03	8.9–10.1	
$1\,^5A_g$	Double[b] excitation valence	9.39	9.61	...	...	...	...	...	...	
$\bar{J}$	Superexcited	...	...	...	...	...	...	11.00 ± 0.04	10.2–11.5	
$n\,^3A_u$	Rydberg	11.37	...	...	...	...	...	...	...	
$n\,^1A_u$	Rydberg	13.48	...	...	...	...	...	...	...	

[a]Reference 19.
[b]Reference 2.
[c]Reference 8.
[d]Reference 29.
[e]Reference 9.
[f]Reference 20.
[g]Reference 7.
[h]0–0 band.
[i]References 22, 23.
[j]From Fig. 9 in Ref. 23.
[k]See Sec. 4.5 for discussion about assignment of these bands.
[l]These band limits were determined by a least squares fit and extrapolation, following the deconvolution procedure described in Sec. 4.3.

gestive[30] of a spin forbidden transition.

Moore[9] observes states at 3.2 and 4.9 eV energy loss in the He^+ spectrum but not in the H^+ spectrum, and suggests that both are singlet → triplet transitions. In addition, peaks are observed in the energy loss spectra for both ions at 6.1 and 7.3 eV.

These results are included as part of Table I.

3. EXPERIMENTAL METHODS

The electron impact spectrometer used in this study is the one described by Kuppermann *et al.*,[11] with the exception of detector modifications. A Spiraltron electron multiplier has replaced the previous discrete dynode multiplier. The pulse amplifier and discriminator is a prototype design.

Instrument purity (99.5% minimum) grade 1,3-butadiene, from the Matheson Co., was used without further purification. The gas in the scattering chamber was maintained at a normal pressure of about 5×10^{-3} torr as indicated by an uncalibrated ion gauge. The instrumental resolution, defined as the full width at half-maximum of the elastic peak, was set at 0.15 eV. Relatively low resolution was used because little vibrational fine structure was observed even in optical studies. The incident electron beam was about 6×10^{-8} A at all three impact energies studied. At each energy loss, the electron pulse count is accumulated into one of the 1024 channels of a Nuclear Data multichannel-scaler, and repetitive energy loss scans are made. An energy-loss region 10 eV wide was scanned in about 100 sec. Total data accumulation times of 4 to 6 h were used at each scattering angle.

The observed intensities in the energy-loss spectra at different angles must be corrected for the angular dependence of the scattering volume before meaningful comparisons between them can be made.

After a spectrum is obtained at a given impact energy and scattering angle, the data are punched out on paper tape, transferred onto magnetic tape, and processed by computer. The processing consists of subtraction of background, averaging over neighboring channels (usually 5) for data smoothing, location of bands and their maxima, band deconvolution when desirable and feasible, and calculation of areas under the bands and of area ratios. This procedure is repeated at each impact energy, for different scattering angles over the angular range studied. The impact energies reported in this paper have not been corrected for contact potential. However, in past studies with this apparatus, such corrections were found to be less than 0.1 eV. The energy-loss scale is accurate to better than 0.01 eV.

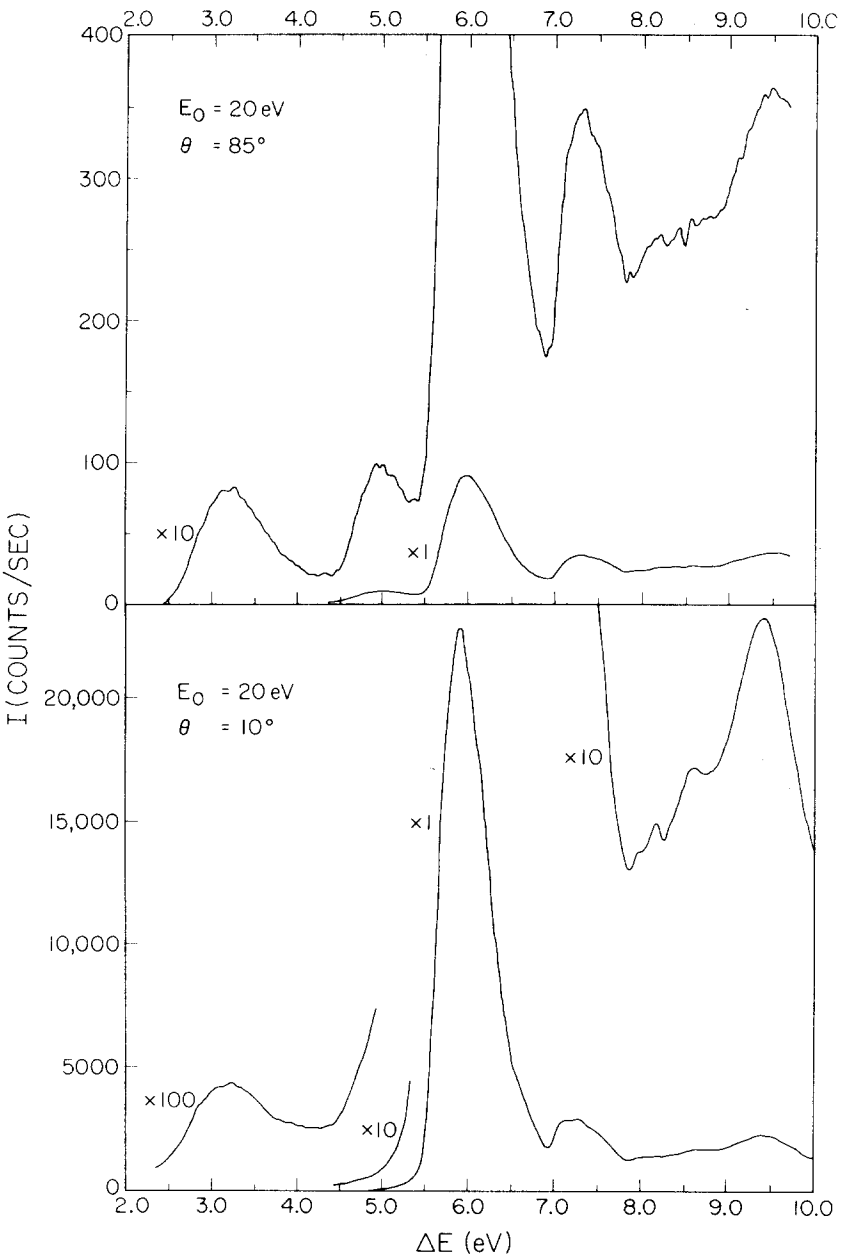

FIG. 1. Electron energy-loss spectrum of 1, 3-butadiene at scattering angles of 10° and 85°; 20 eV incident electron energy; 3×10^{-9} A incident beam current; 4×10^{-3} torr pressure reading from an uncalibrated ion gauge.

4. RESULTS AND DISCUSSION

Table I summarizes the results obtained in our experiments[31] as well as the more pertinent experimental and theoretical studies.

4. 1 The $1\,^3B_u$ State

Figure 1 shows that the first inelastic feature in butadiene has an apparent onset of about 2. 5 eV, a maximum at 3. 22 ± 0. 04 eV (the uncertainty refers to a standard deviation), and an apparent end at about 4. 5 eV. Figure 2 displays the ratio of the area under this peak to that under the $1\,^1B_u$ peak at 5. 92 eV, as a function of scattering angle for each impact energy used.

This ratio, obtained using the deconvolution procedure described in Sec. 4. 3, increases by a factor of about 40 over the angular range 10° to 85°. Such an increase is typical of a spin-forbidden excitation. Comparison with the theoretical results discussed earlier shows that the upper state is the $1\,^3B_u$. The most recent calculations place the vertical excitation at 3. 45[2] or 3. 24 eV.[19] If the observed experimental intensity maximum corresponds to a vertical[24] transition, then the agreement between theory and experiment is good.

At each scattering angle, the cross ratio at 55 eV is less than that at 20 eV. If this behavior extends to 180°, the ratio of the corresponding total

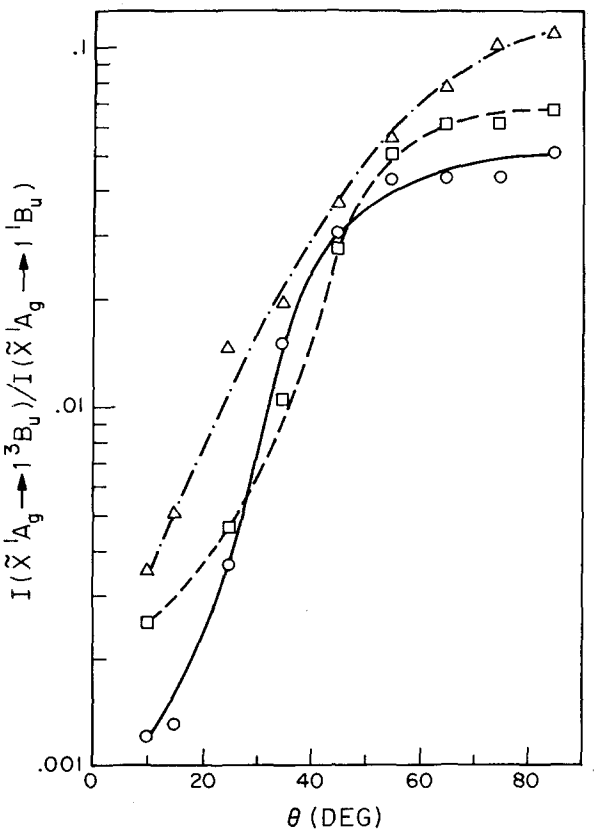

FIG. 2. Ratio of the intensity of the $\tilde{X}\,^1A_g \rightarrow 1\,^3B_u$ transition to that of the $\tilde{X}\,^1A_g \rightarrow 1\,^1B_u$ transition, as a function of scattering angle, for several incident energies E_0: 20 eV (△), 35 eV (□), and 55 eV (○).

cross sections decreases with increasing impact energy. The total cross section for a spin-forbidden transition generally peaks slightly above threshold and then decreases rapidly with increasing impact energy.[32] The spin-allowed transition total cross section, however, increases more slowly to a broad maximum at 50 to 100 eV beyond threshold, and then slowly decreases.[33] Thus, in the present impact energy range, one expects to see the total cross section ratio of spin-forbidden to spin-allowed transitions decrease with increasing impact energy. This is consistent with our observations for the contributions to the total cross sections from the 10° to 85° angular range.

4.2. The 3.8 eV Region

Careful examination of Fig. 1 and the 30 or more spectra upon which this study is based fails to indicate a peak or even a significant slope break on the high energy-loss side of the 1^3B_u state, in agreement with Moore.[9] It is possible that the 3.8 eV feature which is reported by Brongersma *et al.*[8] has a negligible excitation cross section at these impact energies. However, it is difficult to understand why a transition which is presumably a singlet → triplet excitation should have a radically different energy dependence from that of the $\tilde{X}\,^1A_g \rightarrow 1\,^3B_u$ transition. Furthermore, the accurate configuration interaction calculations summarized earlier place only two triplet states arising from $\pi \rightarrow \pi^*$ excitations below about 6 eV. Since we observe an additional triplet state at 4.91 eV, as discussed in the next section, we are unable to offer any further explanation concerning a possible state at 3.8 eV.

4.3 The $1\,^3A_g$ State

The second inelastic feature in Fig. 1 peaks at 4.91 ± 0.03 eV, with an onset of about 4.0 eV, and an apparent end beyond 5.5 eV. Because of the partial overlap between the $\tilde{X}\,^1A_g \rightarrow 1\,^3A_g$ and $\tilde{X}\,^1A_g \rightarrow 1\,^1B_u$ transitions, especially at low scattering angles, we found it necessary to adopt a deconvolution procedure to separate them. The shapes of all bands are taken to be independent of angle, an assumption which has been shown to be valid for low energy electron impact spectroscopy.[11b] The band shape of the optically allowed transition is then determined from a suitable low angle reference spectrum, for which the relative contribution of the $\tilde{X}\,^1A_g \rightarrow 1\,^3A_g$ process is small. An angle-dependent scaling factor is obtained from the ratio of the allowed state peak heights at the reference angle and at the higher angle for which the deconvolution is being performed. The scaled low angle reference spectrum is then subtracted from the high angle spectrum, thereby furnishing the deconvoluted forbidden band. In addition, the high energy tail of the $\tilde{X}\,^1A_g \rightarrow 1\,^3B_u$ transition is estimated by a least-squares extrapolation of the part of the band not overlapped by the $\tilde{X}\,^1A_g \rightarrow 1\,^3A_g$ transition.

Figure 3 is a plot of the angular dependence of the ratio of the area under the $\tilde{X}\,^1A_g \rightarrow 1\,^3A_g$ feature to that under the $\tilde{X}\,^1A_g \rightarrow 1\,^1B_u$ transition for three impact energies. The characteristic increase of this ratio with scattering angle, its decrease with increasing impact energy, and the similarity to the results for the $\tilde{X}\,^1A_g \rightarrow 1\,^3B_u$ transition in Fig. 2 all confirm the singlet → triplet nature of the 4.91 eV transition. Comparison with theoretical calculations indicates that the upper state is indeed the $1\,^3A_g$. Hosteny *et al.*[2] calculate the vertical excitation energy of this state to be 5.04 eV, while Shih *et al.*[19] place it at 4.95 eV, in very good agreement with our 4.91 ± 0.03 eV value.

Butadiene might be expected to have a large quenching cross section for Hg resonance radiation, because of the similar excitation energies of its $1\,^3A_g$ state and the $^3P_1$ state of Hg (4.89 eV). The measured[34a] cross section (36 Å^2) is indeed large, in contrast to the value[34b] (3.0 Å^2) for *n*-butane, a

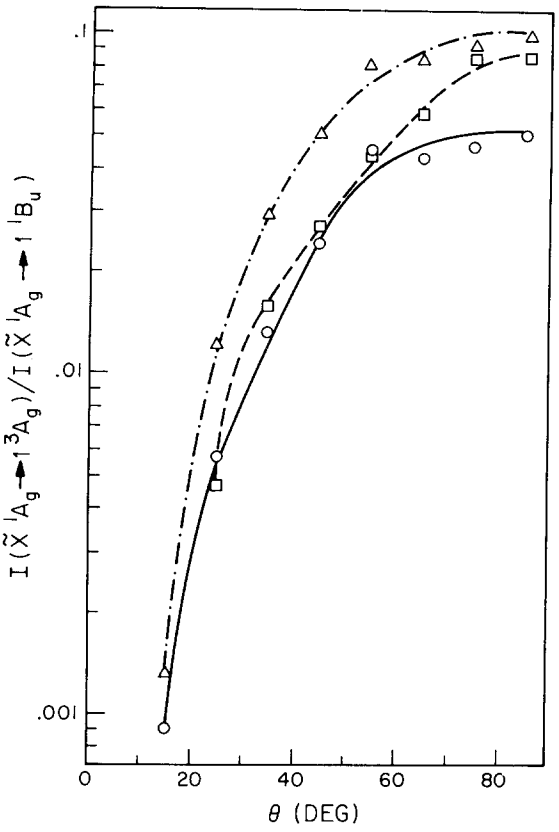

FIG. 3. Same as Figure 2 for ratio of intensities of $\tilde{X}^1A_g \rightarrow 1^3A_g$ and $\tilde{X}^1A_g \rightarrow 1^1B_u$ transitions.

molecule of similar size and molecular weight. It must be noted, however, that general principles which can be used to correlate the magnitude of quenching cross sections with properties of the quenching molecule are scarce.[35] Darwent *et al.*[34a] observed experimentally that most of the olefins, diolefins, and acetylenic compounds studied show similar large quenching cross sections. Callear and Cvetanovic[36] have suggested that, in ethylene, a vibrationally excited triplet state is formed during the energy transfer process. This may also be an important part of the quenching mechanism in the case of other unsaturated hydrocarbon molecules.[37] Singlet → triplet maximum intensity excitation energies have since been observed within ±0.3 eV of 4.9 eV for ethylene,[7,38] acetylene,[39] benzene,[40] and now butadiene, and the large measured quenching cross sections (26 Å^2,[34a] 23 Å^2,[34a] 39.4 Å^2,[41] and 36 Å^2,[34a] respectively) show that energy transfer to these triplet states may be an important part of the quenching mechanism. One should be careful to note, however, that one cannot preclude the possibility that lower triplet states, when they do exist (as is the case for butadiene and benzene), can be significant contributors to the quenching mechanism.

4.4 The $1\ ^1B_u$ State

The strongest feature observed in our spectra is the $\tilde{X}^1A_g \rightarrow 1^1B_u$ transition peaking at 5.92 eV, in good agreement with optical studies.[22,23] At the resolution used in the present experiments, we do not observe the vibrational features which are seen optically.[20–23] Comparison with the theoretical calculations discussed previously, the strong intensity of this transition, and the fact that the differential cross section is strongly forward peaked show that the upper state is an optically allowed singlet. This is consistent with Mulliken's[12] assignment of this state as the 1^1B_u.

Much discussion[10,42] has involved the location of the 0-0 band of the $\tilde{X}^1A_g \rightarrow 1^1B_u$ transition. Examination of Fig. 1 shows that the overlap between the $\tilde{X}^1A_g \rightarrow 1^1B_u$ and the $\tilde{X}^1A_g \rightarrow 1^3A_g$ transitions makes it very difficult to locate the 0-0 band based on these studies. An accurate deconvolution depends on knowing the exact shape of the $\tilde{X}^1A_g \rightarrow 1^1B_u$ band without the influence of the $\tilde{X}^1A_g \rightarrow 1^3A_g$ band. However, careful study of the low angle spectra, where the $\tilde{X}^1A_g \rightarrow 1^1B_u$ transition is very strong relative to the $\tilde{X}^1A_g \rightarrow 1^3A_g$ transition, shows a finite contribution at 5.0 eV from the 1^1B_u state. Recognition of the incident beam energy spread allows placement of an upper bound of 5.1 eV on the location of the $\tilde{X}^1A_g \rightarrow 1^1B_u$ 0-0 band.

4.5. The 7.28 eV Region

Another feature, shown in Fig. 4, is observed between 6.9 eV and 7.8 eV with peaks at 7.09, 7.28, and 7.46 eV. The angular dependence of the

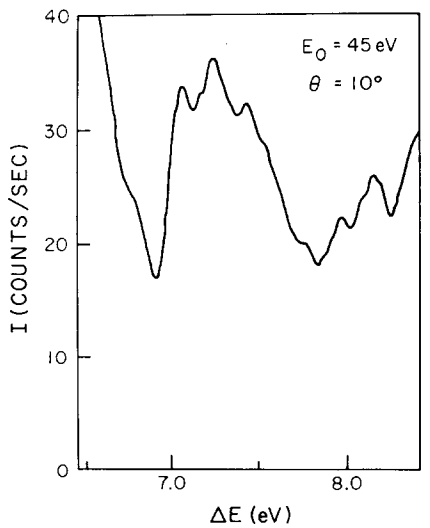

FIG. 4. Electron energy-loss spectrum of 1,3-butadiene in the 6.5 to 8.5 energy loss range at a scattering angle of 10°; 45 eV incident beam energy; 4×10^{-3} torr pressure reading from an uncalibrated ion gauge.

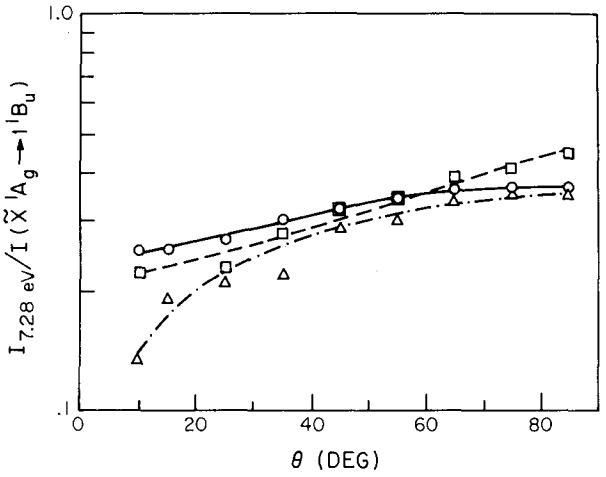

FIG. 5. Same as Figure 2 for ratio of intensities of the 7.28 eV band system and the $\tilde{X}^1A_g \rightarrow 1^1B_u$ transition.

ratio of the area under this transition to that under the $\tilde{X}^1A_g \rightarrow 1^1B_u$ transition is shown in Fig. 5. Although this transition was previously identified[1] as $\tilde{X}^1A_1 \rightarrow {}^1A_1$ of *s-cis* butadiene or $\tilde{X}^1A_g \rightarrow {}^1A_g$[14b] of *s-trans* butadiene, its assignment to the $\tilde{X}^1A_g \rightarrow 2^1B_u$ transition of *s-trans* butadiene is also consistent with the following analysis of both previous and present experimental results.

The optical absorption intensity of the 7.28 eV band system has been estimated[1] to be 20% of that of the 5.92 eV band system. This corresponds to an oscillator strength (f) of about 0.1. Mulliken[1] suggested that if the oscillator strengths for $\pi \rightarrow \pi^*$ transitions were the same in the *s-cis* and *s-trans* forms of butadiene, then this would indicate the presence of about 20% *s-cis* molecules at room temperature. Chemical[43] and thermodynamic[44] studies show, however, that the actual percentage of *s-cis* molecules at this temperature is 3% to 7%. The observed intensity is too high to be produced by *s-cis* molecules in such a concentration and, therefore, the band system must be attributed to a transition of *s-trans* butadiene. Price and Walsh[20] suggested that it is either an $\tilde{X}^1A_g \rightarrow {}^1A_g(N \rightarrow V_2)$ transition, occurring in violation of the optical electric dipole selection rule, or that it has some other assignment, such as a transition to a Rydberg state. The $\tilde{X}^1A_g \rightarrow {}^1A_g$ assignment was also adopted by Pariser and Parr.[14b]

If the $\tilde{X}^1A_g \rightarrow {}^1A_g$ assignment is correct, then this optically forbidden transition is both electric quadrupole-and magnetic dipole-allowed. Its intensity, however, in the absence of vibronic coupling, is far too high for this type of transition.[45] Therefore, this assignment requires that vibronic interaction play a significant role in this transition. The observed vibrational spacing of 1500 ± 150 cm^{-1} in the 7.28 eV band system must be associated with vibrations of the upper electronic state of b_u symmetry in order for this state to be vibronically[46] coupled to the optically allowed 1^1B_u state. It is not possible at present to state whether or not such a symmetry assignment for these vibrations is correct. The C = C stretch vibrational spacing[47] for the ground electronic state $\tilde{X}^1A_g$ is 1599 cm^{-1} for vibrations of b_u symmetry and 1643 cm^{-1} for those of a_g symmetry. For the 1^1B_u state, the C = C vibrations of b_u symmetry are not observed, whereas those of a_g symmetry have a spacing of 1440 cm^{-1}.[20] On this basis, the 1500 ± 150 cm^{-1} upper state spacing is consistent with either a b_u or a_g symmetry and therefore the $\tilde{X}^1A_g \rightarrow {}^1A_g$ assignment of the 7.28 eV transition cannot be excluded.

Additional evidence on the nature of the 7.28 eV transition comes from an analysis of the intensity variation of the electron impact spectrum with scattering angle in this region. The angular dependence of the ratio of the differential cross section of this transition to that of the $\tilde{X}^1A_g \rightarrow 1^1B_u$ transition (see Fig. 5) is characterized by its relative constancy, within a factor of 2 to 3, over the angular range of this study. There are only a few electron impact studies[11b] available of cross section ratios for which both upper electronic states have been identified optically, both transitions are spin-allowed, and the molecule has inversion symmetry. Two possible generalizations are consistent with those studies. When both transitions satisfy the inversion symmetry selection rule ($g \rightarrow u$), the cross section ratio changes by a factor of 3 or less over the entire angular range from 10° to 85°, and shows only small oscillations, if any. However, when the numerator of the ratio corresponds to a $g \rightarrow g$ transition and the denominator to a $g \rightarrow u$ transition, stronger oscillations appear and the relative change in the ratio is in the range from 4 to 7. If these generalizations are valid, the behavior of the cross section ratio for the transitions being considered in butadiene is indicative of an inversion symmetry-allowed transition, e.g., $\tilde{X}^1A_g \rightarrow 2^1B_u$ or $\tilde{X}^1A_g \rightarrow {}^1A_u$. The conclusion from these arguments is that the $\tilde{X}^1A_g \rightarrow {}^1A_g$ assignment may be incorrect, in agreement with a recent suggestion by Shih *et al.*[19] and by Dunning.[2b]

Considering the electric dipole-allowed possibilities, we find that two arguments favor a B_u assignment. First, the spacing between the two lowest B_u states in the configuration interaction calculation[19] which allows for some relaxation of the sigma core is 1.38 eV, in excellent agreement with our observed spacing of 1.36 eV between the peaks of the 1^1B_u and 7.28 eV bands. Second, the theoretical analysis[2,19] of the two lowest B_u excited

states indicates that both have a similar diffuse nature. It is expected, therefore, that the vibrational frequencies should approach those of the ground state of the butadiene positive ion. The experimentally observed value of 1500 ± 150 cm^{-1} for the C=C stretch of the 7.28 eV band system is similar to the corresponding optical value for the 1^1B_u state (1440 cm^{-1})[20] and to the measured values for the positive molecular ion (1400 cm^{-1},[48] 1500 cm^{-1},[49] and 1520 cm^{-1} [50]) and, as mentioned previously, is reduced slightly from its value in the $\tilde{X}\,^1A_g$ ground state, as expected for a Rydberg-like transition.

In summary, assignment of the 7.28 eV band system entirely to an $\tilde{X}\,^1A_g \rightarrow {}^1A_g$ transition is not necessarily correct. This band system may instead be wholly or at least partly due to the $\tilde{X}\,^1A_g \rightarrow 2\,^1B_u$ transition.

4.6. Features above 8 eV

Sharp peaks are observed at 8.00 and 8.18 eV, as shown in Figs. 1, 4, and 6, in good agreement with the optical values of Price and Walsh,[20] who analyzed the spectra and showed that these are the first members of two separate Rydberg series.

Two additional broad features are seen at 9.50 eV and 11.00 eV (Figs. 1 and 6), beyond the first ionization potential of 9.07 eV. The first state was seen optically[20] and by fixed angle electron impact,[29] while the second feature has not been reported previously.

5. DISCUSSION OF THE SENSITIZED PHOTOCHEMISTRY OF BUTADIENE

Photochemical experiments[51] have been performed in solution using carbonyl sensitizers having triplet state energies of 3.2 eV and below to cause dimerization reactions of butadiene. The precursor state in these cycloaddition reactions is identified[51] as the T_1 triplet (i.e., $1\,^3B_u$) state. This is the only state which is accessible to the molecule with the available excitation energies.

Before discovery of the $1\,^3A_g$ state at 4.91 eV maximum intensity transition energy, the nature of the triplet state involved in the Hg ($^3P_1$)-sensitized photochemistry of butadiene was a matter for puzzlement.[10] According to the currently accepted theory,[52] developed for the solid state, the rate of triplet–triplet energy transfer due to exchange interactions is dependent upon the energy overlap of the $S_0 \rightarrow T$ absorption spectrum of the acceptor and the phosphorescence spectrum of the donor. Recent studies[53,54] have suggested that a similar spectral overlap criterion applies in the gas phase. We would expect, therefore, that electronic energy transfer from Hg ($^3P_1$) into T_1 of butadiene would be an unfavorable process, because of the negligible overlap of the $S_0 \rightarrow T_1$ absorption with the Hg ($^3P_1 \rightarrow {}^1S_0$) emission line. However, since the maximum absorption into the T_2 state ($1\,^3A_g$) of butadiene occurs near the energy of the Hg 2537 Å emission line, triplet–triplet energy transfer into this state may well be more efficient. It is important to note that the energy overlap criterion is based upon the assumption that the transitions involved are governed by Franck–Condon factors. There is some evidence,[55] however, that certain energy transfer processes occur via "nonvertical" excitations. Although this conclusion has been challenged,[56] we cannot exclude the possibility that Hg ($^3P_1$)-photosensitization of butadiene occurs through nonvertical excitation of the T_1 state, but it seems probable that the mechanism involves, at least in part, the population of the T_2 state. It can then rapidly radiate and/or internally convert (with a lifetime of the order of 10^{-9} sec or less) to the T_1 state, from which reaction may occur.

6. CONCLUSIONS

The results presented in this paper and an analysis of earlier work lead to four major conclusions. The lowest electronic state of *s-trans* 1,3-butadiene is the $1\,^3B_u$ state with a maximum intensity at 3.22 eV. No state is observed at 3.8 eV in this study in contrast with earlier experiments, but in agreement with ion impact studies. A second triplet, the $1\,^3A_g$ state, is observed at a maximum intensity energy loss of 4.91 eV. This value suggests that the $1\,^3A_g$ state may play a significant role in populating the triplet manifold of 1,3-butadiene in the gas phase Hg($^3P_1$)-sensitized photochemistry of this molecule. Finally, it is argued that the

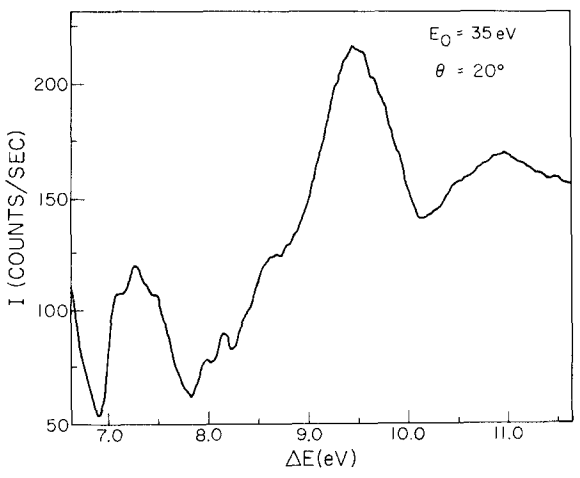

FIG. 6. Electron energy-loss spectrum of 1,3-butadiene in the 6.8–11.5 energy-loss range at a scattering angle of 20°; 35 eV incident beam energy; 4×10^{-3} torr pressure reading from an uncalibrated ion gauge.

band system with a maximum intensity at 7.28 eV need not be assigned solely to an $\tilde{X}\,^1A_g - {}^1A_g$ transition, as previously believed, but may wholly, or at least in part, be due to the $\tilde{X}\,^1A_g - 2\,^1B_u$ transition.

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